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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] It is related with a suitable laminating form solid-state capacitor to use this invention for electronic equipment, especially the smoothing circuit section of a power outlet, and its manufacture technique.

[Description of the Prior Art] In recent years, in connection with a miniaturization and the high-reliability of electronic equipment, and carrying-izing, a miniaturization, highly-efficient-izing, and reinforcement of the electronic parts used for this are progressing. The development of the small mass solid-state capacitor which is a low impedance and has a low equivalent-series-resistance value (low ESR value) as a capacitor especially used for the output smoothing circuit section of power is desired.

[0003] The aluminum solid-state electrolytic capacitor which makes a conductive functional poly membrane the quality of the electric field is a low impedance by carrying out the laminating of the capacitor element veneer, and the laminating form solid-state capacitor of ** [many] which can be considered as the small mass capacitor which has a low equivalent-series-resistance value is proposed.

[Problem(s) to be Solved by the Invention] Since an anodic oxide film existed in the fraction into which the capacitor element veneer laminates the laminating form solid-state capacitor proposed now in the manufacture technique, in the electric welding process, laminating number of sheets was [2-3 sheets] limits. Moreover, the technique of carrying out the laminating of the 2-3 or more sheets was technically difficult, and became the cost rise, and the problem are scarce was also in utilization.

[0005] Moreover, in the conventional solid-state capacitor, since etching processing of the whole front face of metal substrates, such as aluminum, is carried out, it is split-face-ized and it will be etched by the anode plate fraction of the capacitor element veneer, when the laminating of the capacitor element veneer was carried out, there was a problem that the laminating of this anode plate fraction that became thin became difficult.

[0006] this invention was made in view of the above-mentioned point, and makes [many] laminating number of sheets, and it aims at large-capacity-izing being possible, and an anode plate fraction not becoming thin by etching processing, and offering the laminating form solid-state capacitor with an easy laminating process, and its manufacture technique.

[0007]

[Means for Solving the Problem] In order to solve the above-mentioned technical probrem invention given in this application claim 1 While an insulating resin layer is formed in the front face of the boundary section of the fraction used as the anode-terminal section of the plate-like metal base which can form an anodic oxide film, and the fraction in which the capacitor section is formed Split-face-ize the front face of the fraction used as this capacitor section, and into this split-face-ized fraction An anodic oxide film, Form a conductive functional poly membrane and a conductor layer, form the capacitor section, and it considers as the capacitor element veneer. Two or more sheets laminating of the capacitor element veneer is carried out, and it is characterized by joining the conductor layers of the capacitor section with an electric conduction paste, joining the plate-like metal bases of the anode-terminal section by the electric spot welding or laser welding, and constituting a laminating form solid-state capacitor element.

[0008] Moreover, invention given in this application claim 2 leaves the fraction used as the capacitor section to the front face of the plate-like metal base which can form an anodic oxide film, forms an insulating resin layer and masks other fractions. Carry out etching processing of the fraction which has not carried out this masking, split-face-ize it, and into this split-face-ized fraction An anodic oxide film, Form a conductive functional poly membrane and a conductor layer one by one, and the capacitor section is formed. Furthermore, except for the fraction which adjoins the capacitor section, remove the masked insulating resin layer, expose a plate-like metal base, and the capacitor element veneer is manufactured. Two or more sheets laminating of the capacitor element veneer is carried out, and the conductor layers of the capacitor section are joined with an electric conduction paste, the plate-like metal bases of a fraction which removed the insulating resin are joined by the electric spot welding or laser welding, and it is characterized by considering as a laminating form solid-state capacitor element.

[0009] Moreover, while invention given in this application claim 3 forms a thick-film oxide film on anode in the front face of the boundary section of the fraction used as the anode-terminal section of the plate-like metal base which can form an anodic oxide film, and the fraction in which the capacitor section is formed Split-face-ize the front face of the fraction used as the capacitor section, and on the front face of this split-face-ized fraction An anodic oxide film, It considers as the capacitor element veneer as capacitor section in which the conductive functional poly membrane and the conductor layer were formed. Two or more sheets laminating of the capacitor element veneer is carried out, and the conductor layers of the capacitor section are joined with an electric conduction paste, the plate-like metal bases of the anode-terminal section are joined by laser welding, and it is characterized by constituting a laminating form solid-state capacitor element.

[0010] Moreover, on the front face of the plate-like metal base which can form an anodic oxide film, invention given in this application claim 4 forms an insulating resin layer, and masks the fraction used as the capacitor section. The insulating resin layer of the fraction which formed the thick-film oxide-film-on-anode layer in the fraction which has not carried out this masking, and masked it is removed. Carry out etching processing of this fraction, split-face-ize it, and on the front face of this split-face-ized fraction An anodic oxide film, Form a conductive functional poly membrane and a conductor layer one by one, and the capacitor section is formed. Furthermore, separate the fraction which cuts

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 the predetermined position of the plate-like metal base of the thick-film oxide-film-on-anode formation section which follows the capacitor section, and contains this capacitor section from a plate-like metal base, and the capacitor element veneer is manufactured. Two or more sheets laminating of the capacitor element veneer is carried out, and the conductor layers of the capacitor section are joined with an electric conduction paste, the cut surfaces of a plate-like metal base are joined by laser welding, and it is characterized by considering as a laminating form solid-state capacitor element.
 - [0011] Moreover, invention given in this application claim 4 is characterized by performing pressure-proof enhancement processing and enhancement processing in anti-corrosion to a thick-film oxide film on anode.
 - [Embodiments of the Invention] Hereafter, the example of this invention is explained based on a drawing. Drawing 1 is drawing showing the manufacturing process of the laminating form solid-state capacitor of this invention. As shown in drawing 1 (a), it leaves the fraction 2 used as the capacitor fraction of this plate-like metal base 1, using an aluminum plate (or foil) as a plate-like metal base 1 which can form an anodic oxide film, and other fractions 3 (anode-terminal section) are masked in the insulating resin layers 4, such as an epoxy resin.
 - [0013] Then, etching processing of the front face of the fraction 2 used as the capacitor fraction of the plate-like metal base 1 is carried out, it is split-face-ized, and on it, as shown in drawing 1 (b), the capacitor section 5 is formed. The capacitor section 5 is the structure which formed the anodic oxide film 5-1, the conductive functional poly membrane 5-2, the graphite layer 5-3, and the silver paste layer 5-4 in the front face of the plate-like metal base 1 split-face-ized as shown in drawing 1 (c) one by one.
 - [0014] An anodic oxide film 5-1 forms the front face of the aluminum plate which is the plate-like metal base 1 with a well-known chemical conversion. As a conductive functional poly membrane 5-2, the polymer layer of heterocycle formula combination of a pyrrole, a thiophene, a furan, etc. is formed by the well-known electrolytic oxidation polymerization, for example. The graphite layer 5-3 carries out being immersed into graphite liquid etc., and is applied and formed on the conductive functional poly membrane 5-2. Moreover, the silver paste layer 5-4 is applied and formed on the graphite layer 5-3. Then, the front face of the plate-like metal base 1 of the fraction which left the predetermined section (boundary section of the capacitor section 5 and the anode-terminal section 3) which follows the capacitor section in the insulating resin layer 4, removed the edge as shown in drawing 1 (d), and was removed is exposed, and it considers as the capacitor element veneer 6. [0015] As shown in drawing 1 (e), two or more sheets (drawing three sheets) laminating of the capacitor element veneer 6 of the above-mentioned configuration is carried out, the silver paste layers of the capacitor section 5 are joined with a silver paste, plate-like metal base 1 comrades of the anode-terminal section 3 are joined by the electric spot welding or laser welding, and the laminating form solid-state capacitor element 7 is manufactured.
 - [0016] The fraction which serves as the anode-terminal section 3 of the plate-like metal base 1 by constituting the laminating form solid-state capacitor element 7 as mentioned above is thick with the smooth side by which etching processing is not carried out, and since the anodic oxide film is not formed, it is easily joinable by the electric spot welding or laser welding, therefore -- many -- the mass laminating form solid-state capacitor element which can carry out the laminating of the sheets [several] capacitor veneer is obtained
 - [0017] An anode plate external terminal is attached in the anode-terminal section 3 for the cathode external terminal which is not illustrated among the capacitor section 5 of the laminating form solid-state capacitor element 7 of the above-mentioned configuration, sheathing, such as a predetermined resin, is performed, and it considers as a laminating form solid-state capacitor.
 - [0018] Drawing 2 is drawing showing other manufacturing processes of the laminating form solid-state capacitor of this invention. As shown in drawing 2 (a), it leaves the fraction 2 used as the capacitor fraction of this plate-like metal base 1, using an aluminum plate (or foil) as a plate-like metal base 1 which can form an anodic oxide film, and the thick-film oxide film on anode 10 is formed in other fractions 3 (anode-terminal section). In this case, the edge of the anode-terminal section serves as exposed-surface 1a of the plate-like metal base 1. [0019] Then, etching processing of the front face of the fraction 2 used as the capacitor fraction of the plate-like metal base 1 is carried out, it is split-face-ized, on it, as shown in drawing 2 (b), the capacitor section 5 is formed, and the capacitor element veneer 11 is manufactured. The capacitor section 5 is the structure which formed the anodic oxide film 5-1, the conductive functional poly membrane 5-2, the graphite layer 5-3, and the silver paste layer 5-4 in the front face of the plate-like metal base 1 split-face-ized as shown in drawing 2 (c) one by one. The formation technique of these anodic oxide films 5-1, the conductive functional poly membrane 5-2, the graphite layer 5-3, and the silver paste layer 5-4 is the same as that of the case of drawing 1, and an explanation is omitted.
 - [0020] As shown in drawing 1 (d), two or more sheets (drawing four sheets) laminating of the capacitor element veneer 11 of the above-mentioned configuration is carried out, the silver paste layers of the capacitor section 5 are joined with a silver paste, and the laser-welding section 12 is formed in exposed-surface 1a of the end face of the plate-like metal base 1 of the anode-terminal section 3, it joins to it, and the laminating form solid-state capacitor element 13 is manufactured.
 - [0021] since the laser-welding section 12 is formed in exposed-surface 10a of the edge in which the fraction which serves as the anode-terminal section 3 of the plate-like metal base 1 by constituting the laminating form solid-state capacitor element 13 as mentioned above is thick with the smooth side by which etching processing is not carried out, and the thick anodic oxide film 10 is not formed and it joins to it -- many -- the mass laminating form solid-state capacitor element 13 with the easy laminating of the sheets [several] capacitor veneer is obtained
 - [0022] An anode plate external terminal is attached in the anode-terminal section 3 for the cathode external terminal which is not illustrated among the capacitor section 5 of the laminating form solid-state capacitor element 13 of the above-mentioned configuration, sheathing, such as a predetermined resin, is performed, and it considers as a laminating form solid-state capacitor.
 - [0023] Drawing 3 (a) to (d) is drawing showing the manufacturing process of the above-mentioned capacitor element veneer 11. As shown in drawing 3 (a), the aluminum plate (foil) with a front face smooth as a plate-like metal base 1 is prepared, and the hole 14 which becomes this plate-like metal base 1 with the flank of the anode-terminal section 3 (refer to the drawing 2) of a capacitor is pierced. Then, as shown in drawing 3 (b), a photoresist layer 15 is formed in the fraction which forms the capacitor section 5. As shown in drawing 3 (c) in this status, the thick-film anodic oxide film 16 is formed in the fraction in which a photoresist layer 15 is not formed.
 - [0024] Into the aqueous solutions, such as a nitric acid, a sulfuric acid, a phosphoric acid, and a chromic acid, formation of the above-mentioned thick-film anodic oxide film 16 is immersed, and anodic oxidation of the plate-like metal base 1 in which the photoresist layer 15 was formed is carried out, and it forms it. Adipic-acid ammonium etc. performs pressure-proof enhancement processing and processing by pressurization steam sealing on an anti-corrosion disposition as after treatment after formation of this thick-film anodic oxide film 16.
 - [0025] In case it exfoliates and etching processing of the photoresist layer 15 is carried out so that it may mention later by performing this

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pressure-proof enhancement processing and enhancement processing in anti-corrosion, and conductive functional poly membranes, such as the
poly pyrrole layer, are further formed by the electrolytic oxidation polymerization, the thick-film anodic oxide film 16 can be equal to this etching

processing or an electrolytic oxidation polymerization.

[0026] Then, the periphery 17 of the fraction which forms the capacitor section 5 as it exfoliates and a photoresist layer 15 is shown in <u>drawing</u> 3 (d) is pierced, then, the fraction which forms this capacitor section 5 -- etching processing -- carrying out -- a split face ---izing -- the front face -- formation -- it -izing-processes, an anodic oxide film 5-1 is formed, and the conductive functional poly membrane 5-2, the graphite layer 5-3, and the silver paste layer 5-4 are formed further one by one Then, by cutting the fraction {line C of view 3 (d)} which connects the base of a hole 14 and the hole 14, the capacitor element veneer 11 of the cross-section structure shown in <u>drawing 2</u> (b) is completed.

[0027] By manufacturing the capacitor element veneer 11 through the above-mentioned process, a hole 14 is pierced to the aluminum plate which is the plate-like metal base 1, other processes except each process of the punching of formation of a photoresist layer 15 and sublation, and the peripheral 17 turn into the down stream processing in a solution, and a down stream processing becomes easy

and the periphery 17 turn into the down stream processing in a solution, and a down stream processing becomes easy.

[Effect of the Invention] As explained above, as for invention given in this application each claim, the following outstanding effects are acquired.

[0029] (1) the fraction which serves as the anode-terminal section only in the fraction from which the fraction by which invention according to claim 1 is split-face-ized serves as the capacitor section of a plate-like metal base -- with the thickness of a plate-like metal base -- and -- since the anodic oxide film is not formed in a front face -- the plate-like metal bases of this anode-terminal section -- an electric spot welding or laser welding -- easy -- joinable -- many -- it becomes a mass laminating form solid-state capacitor by carrying out the laminating of the sheets several] capacitor veneer

[0030] (2) According to invention according to claim 2, a mass laminating form solid-state capacitor according to claim 1 can manufacture

easily.

[0031] (3) Since according to invention according to claim 3 etching processing of the fraction which forms a thick-film oxide film on anode except for the fraction used as the capacitor section of a plate-like metal base, and serves as the capacitor section is carried out and it is split-face-ized The fraction by which etching processing is carried out turns into only the fraction in which the capacitor section is formed, the plate-like metal bases which removed the thick-film oxide film on anode of this anode plate section since the anode-terminal section was still the thickness of a plate-like metal base -- laser welding -- easy -- joinable -- many -- it becomes a mass laminating form solid-state capacitor by carrying out the laminating of the sheets [several] capacitor veneer

[0032] (4) According to invention according to claim 4, a mass laminating form solid-state capacitor according to claim 3 can manufacture

easily.

[Translation done.]

PATENT ABSTRACTS OF JAPAN

(11) Publication number: 03095910 A

(43) Date of publication of application: 22.04.91

(51) Int. Cl

H01G 9/02 H01G 9/04 H01G 9/24 // C08G 61/12 C09D 5/25

(21) Application number: 01231390

(22) Date of filing: 08.09.89

(71) Applicant:

NIPPON CHEMICON CORP

(72) Inventor:

SHIMADA AKIHIRO YOKOYAMA YUTAKA ANDO SUSUMU

(54) MANUFACTURE OF SOLID ELECTROLYTIC CAPACITOR

(57) Abstract:

PURPOSE: To reduce an increase in a leakage current due to unformed part caused by high conductivity of polypyrrole by masking the unformed part with an insulating material when a solid electrolytic capacitor is manufactured.

CONSTITUTION: For example, an anode foil with leads is used, a connector of the foil to leads is covered with phenol resin, and cured. After this, a cathode foil with leads, and electrolytic sheet are wound, and are carbonized. This is dipped in ethanol solution of the

pyrrole, then dipped in aqueous solution of $(NH_4)_2S_2O_4$, washed, and dried. After steps of dipping in the pyrrol solution to drying are executed ten times, it is resin-sealed, and manufactured as a product to produce a solid electrolytic capacitor.

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庁内整理番号 43公開 平成3年(1991)4月22日 ⑤Int. Cl. 5 識別記号 7924-5E 9/02 3 3 1 H 01 G 3 0 1 7924-5E 9/04 7924-5E 9/24 Α // C 08 G NLJ8215—4 J 8016-4 J C 09 D 審査請求 未請求 請求項の数 3 (全4頁)

図発明の名称 固体電解コンデンサの製造方法

②特 願 平1-231390

②出 願 平1(1989)9月8日

⑩発 明 者 島 田 晶 弘 東京都青梅市東青梅1丁目167番地の1 日本ケミコン株 式会社内

⑫発 明 者 横 山 豊 東京都青梅市東青梅1丁目167番地の1 日本ケミコン株

式会社内

⑫発 明 者 安 藤 進 東京都青梅市東青梅1丁目167番地の1 日本ケミコン株

式会社内

⑪出 願 人 日本ケミコン株式会社 東京都青梅市東青梅1丁目167番地の1

四代 理 人 弁理士 浜田 治雄

明細書

1. 発明の名称 固体電解コンデンサの製造方法

2. 特許請求の範囲

- (1) 表面に酸化皮膜を有する陽極箔と集電陰極箔との間に多孔質セパレータを介在させて参回した柔子を用い、定量的に化学重合を行うことによりポリピロールを参回素子内に含没形成する固体電解コンデンサの製造方法によりないて、未化成部分を絶縁材料でマスクすることを特徴とする固体電解コンデンサの製造方法。
- (2) 絶縁材料を、エポキシ、フェノールまたはシリコーンのような熱硬化性樹脂、スチレンまたはアクリルのような熱可塑性樹脂、ゴム、有機または無機系コート剤並びにテープよりなる群から選択する請求項1記載の固体電解コンデンサの製造方法。
- (3) 塗布、印刷またはボッティングによりマスクを行う請求項1記載の固体電解コンデンサ

の製造方法、

3. 発明の詳細な説明

[産業上の利用分野]

本発明は、導電性高分子であるピロールを 固体電解質として使用する固体電解コンデン サに関し、更に詳しくは、ボリピロールが高 電等度であることに起因する未化成部分によ る漏れ電流の増加を低減させ得る固体電解コ ンデンサの製造方法に関する。

[従来の技術]

 液状の電解質を使用するイオン伝導によるため、高周波領域において著しく抵抗が増大しインピーダンスが増大する。したがって、高周波特性の点では、固体電解コンデンサの方が格段に優れている。

固体電解コンデンサに用いる固体電解質としては、固体電解質自体の導電性や安定性、並びに用いる固体電解質の性質によって規定される電解コンデンサの静電容量(Cap)、誘電正接(tan &)、漏れ電流(LC)、等価直列抵抗(ESR)等の指標から、ポリピロールが最も優れていると考えられる。

ボリピロールを固体電解質として用いる固体電解コンデンサは、例えば、特開昭63-173313号に開示されている。一般に、この種の固体電解コンデンサを製造するを際には、化学的重合および電解重合により陽極箔上にボリピロールの薄膜を形成し、その後この表面に銀ベーストのような導電ペーストを用いて端子を接着して対極リードを取出し、エポ

製造でき、固体電解コンデンサが本来有する 良好な周波数特性等の利点を備え、ポリピロ ールの薄膜表面から対極リードを取出すこと に起因する接着不良による信頼性の問題等を 全く生じない固体電解コンデンサを得ること ができる。

しかしながら、ポリピロールをセパレータ 入りの巻回衆子内に含浸形成することは定量 的に化学重合を行う方法によって可能である が、通常の衆子を使用した場合、箔とリード キシ樹脂等で外装してコンデンサ製品を作製する。このような製造方法によって製造した 固体電解コンデンサは、陰極の取出しに導電 ペーストを使用するため、接着部分の確実性 に不安が残り、信頼性の点で問題が生じる。

基本的には通常の電解液式の電解コンデンサの構造を有し、同時にポリピロールのような固体電解コンデンサの固体電解質を備える固体電解コンデンサを実現できれば、 繁雑な 製造工程を伴わない簡便な製造方法によって

との取付け部や箔のエッジのような未化成部 分による漏れ電流が大きい。これは、ポリピロールが高電導度であることによる。

[発明が解決しようとする課題]

本発明は、導電性高分子であるピロールを 固体電解質として使用する固体電解コンデン サにおいて、ポリピロールが高電導度である ことに起因する未化成部分による漏れ電流の 増加を低減させ得る固体電解コンデンサの製 造方法を提供することを目的とする。

[課題を解決するための手段]

本発明によれば、表面に酸化皮膜を有する
陽極箔と集電陰極箔との間に多孔質セパレー
夕を介在させて巻回した素子を用い、定量的
に学重合を行うことによりポリピロールを
巻回衆子内に含浸形成する固体電解コンデンサの製造方法において、未化成部分を絶縁コンデンサの製造方法が提供される。

表面に酸化皮膜を有する陽極箔は、通常は

表面を電解酸化によって酸化皮膜誘電体に変えたアルミニウムフィルムとし、集電陰極箔は、通常は未化成アルミニウムフィルムとする。

陽極箔および陰極箔は、リード端子を有するもの、リード端子を有しないもののいずれであってもよい。リード端子を接続する際は、溶接、ステッチ等の通常の接続方法のいずれを使用してもよい。また、銀ペーストのような導電ペーストを用いて端子を接着して対極リードを取出すこともできる。

で含浸用溶媒に溶解した含浸用溶液に浸漬する。含浸用溶媒をァーブチロラクトン、ジメチルホルムアミド、プロピレンカーポネート、エチレングリコール並びにエタノールよりなる群から選択すれば好適である。

その後、酸化剤を5~25重量%の濃度で 化学重合用溶媒に溶解した化学重合用溶液に 浸潤する。酸化剤は、好ましくは

(NH・) 2 S 2 O 3 、F e C 1 3 、並びに H 2 O 2 よりなる群から選択する。化学重合 用溶媒は、好ましくは、水、エチレングリコ ール、ジメチルホルムアミド並びにエタノー ルよりなる群から選択する。化学重合を - 2 0 ~ 3 0 ℃で 5 ~ 3 0 分間行えば好適で ある。

化学重合終了後、必要に応じて100℃で 15分程度乾燥する。前記した含浸用溶液へ の浸渍から乾燥までの工程は、必要に応じて 10回程度繰り返せば好適である。その後樹 脂封止して製品化し、本発明による固体電解 成部分を絶縁材料でマスクすることが重要である。

絶縁材料を、エポキシ、フェノールまたはシリコーンのような熱硬化性樹脂、スチレンまたはアクリルのような熱可塑性樹脂、ゴム、有機または無機系コート剤並びにテープよりなる群から選択すれば好適である。

塗布、印刷またはポッティングによりマス クを行えば好適である。

熱、紫外線または乾燥により塗布した絶縁 材料の硬化を行えば好適である。例えばフェ ノール樹脂を塗布した場合、180℃、20 分程度の条件下で硬化を行えば好適である。

多孔質セパレータをガラス繊維紙、マニラ紙、クラフト紙並びに高分子紙よりなる群から選択すれば好適である。陽極箔、陰極箔並びに電解紙を巻回して衆子を形成後、必要に応じて、例えば350℃で2分間加熱して炭化を行うこともできる。

その後、ピロールを1~50重量%の濃度

コンデンサを得ることができる。

[作用]

前記したように、ポリピロールをセパレータ入りの巻回素子内に含浸形成することは定量的に化学重合を行う方法によって可能であるが、通常の素子を使用した場合、箔とリードとの取付け部や箔のエッジのような未化成部分による漏れ電流が大きい。これは、ポリピロールが高電導度であることによる。

本発明の開示に従い、未化成部分、特にリードの取付け部や箔のエッジを絶縁材料でマスクすることにより、未化成部分に高電導度のボリピロールが付着せず、漏れ電流特性が良好に改善される。

[発明の効果]

本発明によれば、 導電性高分子であるピロールを固体電解質として使用する固体電解コンデンサにおいて、 ポリピロールが高電等度であることに起因する未化成部分による 漏れ電流の増加を低減させ得る固体電解コンデン



サの製造方法、およびその方法によって製造される固体電解コンデンサが提供される。 [実施例]

以下に実施例により本発明を更に詳細に説明するが、本発明は以下の実施例にのみ限定されるものではない。

実施例1

リード付きの陽極箔(22 V,、3 mm× 18 mm)を用い、箔とリードとの接続部にフェノール樹脂を塗布後、180℃で20分間硬化させた。これとリード付き陰極箔(0 V,、3 mm× 25 mm)と電解紙(マニラ紙)とを巻回した後、350℃で2分間炭化させた。これを20%ビロールのエタノール溶液5 m 1 に浸漬し、次いで30%

(NH・) 2 S 2 O 4 の水溶液 1 O μ 2 に没 演し、水洗し、乾燥 (1 O O ℃、15分) した。ピロール溶液への浸漬から乾燥までの工程を計1 O 回行った後、樹脂封止して製品化し、固体電解コンデンサを製造した。

比較例1

箱とリードとの接続部にフェノール樹脂を 塗布せずに巻回素子を作製し、炭化以降は実 施例1と同様にして固体電解コンデンサを製 造した。

実施例 1 および比較例 1 の固体電解コンデンサについて、静電容量(Cap)、誘電正接(tan &)、漏れ電流(LC)並びに等価直列抵抗(ESR)を測定した結果を第 1 表に示す。なお、22 V, で 6 . 3 W V (4 ø×7 I) とした。

第 1 表

方法 Cap(μF) tand LC(μA) ESR(100Kz,Ω) 実験別 14.2 0.021 0.01 0.08 比較別 14.2 0.036 0.19 0.09

この結果から、本発明による固体電解コンデンサは、漏れ電流特性が顕著に向上していることが分る。

特許出願人 日本ケミコン株式会社 出願人代理人 弁理士 浜田治雄派乳